REMARKS

Applicants respectfully request that the finality of this action be withdrawn. Applicants point out that in response to the Official Action 5-10-2002 Applicants argued against both the 102(b) and 103(a) objections on the grounds that none of the references cited by the Examiner contained an reference to a reactive dye. In Paper 6 the Examiner simply restated the arguments from the Original Action and did note address Applicants response of August 7, 2002. Applicants contacted the Examiner by phone in December, 2002 to point out that Applicants arguments had not been addressed and to see if the Examiner had some reference that applicants over looked which teach or suggest a reactive dye. The examiner pointed out the similarity in the chromophore, however the chromophore of acid and direct dyes may be similar it is the reactive functional group, which defines the reactive dye. The Examiner suggested by phone that we should send in a written response to the last action. Applicants hereby submit this response. Applicants respectfully request that the finality of this action be withdrawn and that all the claims be allowed for the reasons outlined below.

Claims 12-15 stand rejected under 35 USC § 102(b) as being anticipated from Mitsubishi Kasei Corporation (JP-06073320). Applicants respectfully traverse this objection. Applicants note, that Claim 12 specifically defines the composition of the current invention as an aqueous solution of at least one reactive dye. A reactive dye must contain by definition at least one substituent capable of forming a covalent bond with the fiber on which it is applied. Please find enclosed a copy of page 386 from Kirk-Othmer, "Concise Encyclopedia of Chemical Technology", which contains the definition for reactive dyes previously given. Further see the enclosed copy of pages 131 – 133 from Aspland, "Textile Dyeing and Coloration", which xplains difference between the chromophores

and reactive functional structures of reactive dye molecules. Please see the dye structures from JP 06-073320, these molecules contain none of the reactive functional structures defined in Aspland, or shown in Examples 2 and 3 on page 10 and 11 of the current application. JP 06-073320 relates to a defined recording liquid containing a water soluble dye such as a direct or acid dye, neither of which forms a covalent bond with the substrate.

Applicants respectfully suggest that the definition of reactive dye would not need to be reiterated in each claim as one of ordinary skill in the art would know immediately the difference between a reactive dye and an acid or direct dye. See bottom of page 2 top of page 3 of paper number 6. Applicants had supplied sufficient examples from technical journals in Applicants response of August 7, 2002 in support of the clear meaning of reactive dye. The Office cannot simply recategorize acid and direct dyes as reactive dyes to support a weak rejection. No attempt has been made by the Office to point out the reactive dyes in the references cited against Applicants except an attempt to call the acid and direct dyes of Mitsubishi Kasei reference reactive dyes. Applicants again respectfully request that these objections be withdrawn and the case allowed.

For the reason listed above Applicants believe that the teaching of Mitsubishi Kasei Corporation fails to make the present invention anticipated, and applicants respectfully request that claims 12-15 be allowed.

Claims 16-22 stand rejected under 35 USC § 103(a) as being obvious from Mitsubishi Kasei Corporation (JP-06073320) in view of Dainippon Ink and Chemical KK (JP 58-198570). This objection is respectfully traversed.

JP-06073320 would not have been obvious based on the argument given above for the allowance of Claims 12-15. The current invention contains at least one reactive dye. JP-06073320 is comprised of a direct dye or an acid dye.

JP 58-198570 relates to pigment compositions and does not contain a reactive dye. Pigments are insoluble in the media of application in this case water. Dainippon teaches the addition of a thickener for pigment dispersions produced by grinding the pigment in the presence of glass beads and defined adjuvants. The current invention is a solution as the reactive dyes are soluble in water. Any considerations about addition of a thickener of the secondary reference in the primary reference are not pertinent because of the different utility and kind of composition in the references: in JP 06-073320 a recording liquid with a water soluble direct or acid dye of the defined formula for ink jet recording; in JP 58-198570 printing compositions which are pigment dispersions produced e.g. by grinding the pigment with beads in the presence of defined adjuvants. No one of ordinary skill in the art would consider that additions made to a water insoluble pigment would be readily adaptable to water soluble dyes. There is no teaching in either reference, or any suggestion that these references can or should be combined.

For the reasons listed above Applicants believe that the teaching of Mitsubishi Kasei Corporation and Dainippon Ink and Chemical KK fail to make the present invention obvious and applicants respectfully request that claims 16-22 be allowed.

Applicants have, for further clarification, attached a translation of JP-06073320 for clarification purposes. Applicants believe that any person of ordinary skill would clearly see that the structures given in the Japanese language copy fail to disclose a reactive dye

Attorney's Docket: 1998CH017
Serial No.: 09/744,784
Art Unit 1751

As the total number of claims does not exceed the number of claims originally paid for, no fee is believed due. However if an additional fee is required, the Commissioner is hereby authorized to credit any overpayment or charge any fee deficiency to Deposit Account No. 03-2060.

Reconsideration and allowance of this application is respectfully requested.

Respectfully submitted,

Scott E. Hanf
Registration No. 38,906

(CUSTOMER NUMBER 25,255)

Clariant Corporation
Industrial Property Department
4000 Monroe Road
Charlotte, NC 28205
New Phone 704 331-7140
New Fax 704 331-7707

Attachment:

Pages 377 and 386 from Kirk-Othmer, "Concise Encyclopedia of Chemical Technology" (3 pages)

pages 131 – 133 from Aspland, "Textile Dyeing and Coloration" (5 pages)

English Translation of JP-06073320 (8 pages)

KIRK-OTHMEI

CONCISE ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY

A WILEY-INTERSCIENCE PUBLICATIO
John Wiley & Son
NEW YORK · CHICHESTER · BRISBANE · TORONTO · SINGAPOR

DYES AND DYE INTERMEDIA

Dyes are intensely colored substances used for the coloration of various substrates, including paper, leather, fur, hair, foods, drugs, cosmetics, waxes, greases, petroleum products, plastics, and textile materials. They are retained in these substrates by physical adsorption, salt or metal-complex formation, solution, mechanical retention, or by the formation of covalent chemical bonds. The methods used for the application of dyes to the substrates differ widely, depending upon the substrate and class of dye. It is by application methods, rather than by chemical constitutions, that dyes are differentiated from pigments. During the application process-dyes lose their crystal structures by dissolution or vaporization. The crystal structures may in some cases be regained during a later stage of the dyeing process. Pigments, on the other hand, retain their crystal or particulate form throughout the entire application procedure. They are usually applied in vehicles, such as paint or lacquer films, although in some cases the substrate itself may act as the vehicle, as in the mass coloration of polymeric materials.

The optical properties of dyes are determined by electronic transitions between the various molecular orbitals of the dye molecules that absorb some, but not all, of the incident radiation. These properties are defined by the terms color, intensity, and brightness. The color, also frequently referred to as . e shade or hue, of a dye is determined by the energ differences between the molecular orbitals. The intensity, strength, (saturation is determined by the probability of the electronic transitio and the amount of dye present. The brightness or purity depends upo the width of the waveband adsorbed by the dye molecules (see Color).

The energy, probability, and distribution of the electronic transition are, to a large extent, governed by the chemical constitution of th molecules. The chemical constitution also determines the other prope ties of a dye, such as the suitability for dyeing a specific substrate an the fastness properties of dyeings produced by the application of the dy to the substrate. A large number of dyes, with widely differing prope ties, is necessary because of the great variety of materials to be dye There are at present some 1200 different commercial dyes manufacture in the United States, and a further 800 are imported. On a worldwi basis, over 8000 chemically different dyes have achieved commerci significance. To assist both the dye users and dye manufacturers, dye are classified into groups in two ways. The first method of classificatio is by chemical constitution, in which the dyes are grouped according t the chromophore or color-giving unit of the molecule. The second metho is based on the application class or use of the dye. The first, from chemical standpoint, satisfies the needs of the manufacturer, and th second is used by the dyer.

Table 1. Usage Classification of Dyes

Class	Major substrates	Method of application	Chemical types	Relevant articles in *ECT*
Not. acid	nylon, wool, silk, paper, inks, and leather	usually from neutral to acidic dyebaths	azo, including premetallized dyes, anthraquinone, triphenylmethane, azine, xanthene, nitro, and nitroso	Azo dyes
azoic components and compositions	cotton, rayon, cellulose acetate, and polyester	fiber impregnated with coupling component and treated with a solution of stabilized diazonium salt	azo	Azo dyes
basic	acrylic, modified nylon and polyester, paper, and inks	applied from acidic dyebaths	methine, diphenylmethane, triarylmethane, azo, azine, xanthene, thiazole, acridine, oxazine, and anthraquinone	Azine dyes; Azo dyes
Not direct	cotton, rayon, paper, leather, and nylon	applied from neutral or slightly alkaline baths containing additional electrolyte	azo, phthalocyanine, stilbene, oxazine, and thiazole	Azine dyes; Azo dyes
disperse	polyester, polyamide, cellulose, acetate, acrylic, and plastics	fine, aqueous dispersions often applied by higher temperature–pressure or lower temperature carrier methods; dye may be padded on cloth and baked on or thermofixed	azo, anthraquinone, nitro, and methine	Azo dyes; Dyes, anthraquinone
fluorescent brighteners	soaps and detergents, all fibers, oils, paints, and plastics	from solution, dispersion or suspension in a mass	stilbene, azoles, coumarin, pyrazine, and naphthalimides	Brighteners, fluorescent
food, drug, and cosmetic	foods, drugs, and cosmetics		azo, anthraquinone, carotenoid, and triarylmethane	Colorants for foods, drugs and cosmetics
mordant	wool, leather, and anodized aluminum	applied in conjunction with chelating Cr salts	azo and anthraquinone	Azo dyes; Dyes, applications and evaluation
natural		applied as mordant, vat, solvent, or direct and acid dyes	anthraquinone, polymethine, ketone imine, flavones, indigoids, quinones, chlorophylls, etc	Dyes, natural
oxidation bases	hair, fur, and cotton	aromatic amines and phenols oxidized on the substrate	aniline black and indeterminate structures	Azine dyes
pigments	paints, inks, plastics, and textiles	printing on the fiber with resin binder or dispersion in the mass	azo, basic, phthalocyanine, quinacridone, oxazine, anthraquinone, and indigoid	Pigments
reactive	cotton, rayon, wool, silk, and nylon	reactive site on dye reacts with functional group on fiber to bind dye covalently under influence of heat and proper pH	azo, anthraquinone and phthalocyanine	Dyes, reactive
solvent	gasoline, varnish, lacquer, stains, inks, fats, oils, and waxes	dissolution in the substrate	azo, triphenylmethane, anthraquinone and phthalocyanine	Azo dyes; Dyes, anthraquinone; Phthalocyanine compounds
sulfur	cotton and rayon	aromatic substrate vatted with sodium sulfide and reoxidized to insoluble sulfur containing products on the fiber	indeterminate structures	Sulfur dyes
vat	cotton, rayon, and wool	H_2O insoluble dyes solubilized by reducing with sodium hydrosulfite, then exhausted on fiber and reoxidized	anthraquinone (including polycyclic quinones) and indigoids	Dyes, anthraquinone

Closely related in chemical structure to the above flavones are substituted dihydropyrans. The most important naturally occurring members are haematin and its leuco form, haematoxylin. These are the principal coloring bodies of logwood (CI Natural Black 1, CI 75290) historically one of the most important natural dyes for dark shades of silk, wool, cotton, leather, wood, and animal bristles, hair, and fur. It is still used extensively in dyeing and tanning leather.

Anthocyanidins (flavylium salts) are glycosides of hydroxylated 2-phenylbenzopyrylium salts. They are usually isolated as the chlorides after hydrolytic fission of the glycoside with hydrochloric acid. The color developed by the plant is determined by the pH of the cell sap. For example, cyanin is red under acidic conditions, violet at neutral pH, and blue under alkaline conditions.

Natural dyes, particularly red shades, have become increasingly important for use in food coloring. With the FDA's withdrawal of FD & C Reds 2 and 4, new sources for food colors have been required. The initial approach by the food-dye industry has been to return to natural dyes such as those of the anthocyanin class.

Alloxan adduct. A yellow dye currently being used as a food colorant is the phosphate salt of riboflavin, vitamin B_2 (see Vitamins). This is found in varying amounts in all plant and animal cells; particularly good natural sources are milk, eggs, malted barley, yeast, liver, kidney, and heart. Excretion of riboflavin in the urine is responsible for the yellow color. Structurally, riboflavin is an alloxan derivative.

Betanin

Another natural dye that is currently being used in food to take the place of the delisted FD & C Reds 2 and 4 is obtained from red beet extracts, *Beta vulgarus*. This is available as beet-juice concentrate, dehydrated beet root, and spray-dried extracts. Red beet root contains both red and yellow pigments of the class betaines; these are quaternary ammonium amino acids. The red bodies are betacyanine pigments of which the major constituent is betanin.

Indigoid Dyes

Two very important natural dyes have the indigoid structure. Indigo, the main product that gives this dyestuff class its name, is still one of the primary dyes of the world, although now made via a synthetic route. Tyrian or royal purple, although no longer in demand, was once the prize sought by the Caesars. The source of Tyrian purple is the purpura shellfish or *Murex Brandaris* found in shallow waters throughout the Mediterranean. Each mollusk contains a few drops of glandular mucous; this fluid at first appears white, but on exposure to light changes to yellow-green and eventually violet or reddish-purple. Natural indigo is obtained from the leaf of *Indigofera tinctoria*, a leguminose, widely distributed in Asia, Africa, and America. The dye is contained only in the leaf of the plant, unlike other vegetable dyes where the coloring matter is also found in the stalk, pods, and twigs. Natural indigo also contains Indigotin (CI 75780), Indirubin (CI 75790), Indigo Brown, Indigo Gluten, and Indigo Yellow (CI 75640).

Carotenoids

Although most color in the visible spectral range is generated by conjugated aromatic ring systems, another class of dyes found in nature obtains its color owing to the presence of long, conjugated double-bond chains (see Terpenoids). These dyes are the carotenoids, the class name being derived from the orange pigment found in carrots, carotene. They are also known as lipochromes because of their solubility and occurrence in fats.

Carotene (Natural Yellow 26; Natural Brown 5; CI 75130) is widely distributed throughout the vegetable and animal kingdoms. The carotenoids have use as colorants in foods and ingested drugs. β-Carotene is permanently listed by the FDA as an FD & C approved colorant (see Colorants for foods, drugs, and cosmetics). At present it is available commercially as a 30% liquid suspension; a 24% semisolid suspension; a 10% beadlet-water dispersion, and a 3% emulsion.

Another carotenoid, extract of annatto, is also used in food coloring. Currently its main use is in dairy products such as butter, margarine, and cheese. Annatto is obtained from the pulpy portion of the seeds of the plant *Bixa orellana*, found in India, Central America, and Brazil.

Saffron is obtained from the pistils of the *Crocus sativus*, a plant that flowers in the fall and is quite different from the common spring variety crocus. The principal chemical constituent of saffron is crocin, the digentiobiose ester of crocetin.

Chlorophyll

Unlike the other natural products discussed in this article, one might not consider chlorophyll in the same class as dyestuffs. This is probably because chlorophyll does not have affinity for the natural fibers, especially cotton and wool, which can be made into wearing apparel. However, if one overlooks this most common dye requirement, chlorophyll is indeed a dyestuff (CI Natural Green 3; CI 75810). It is used extensively for coloring soaps, resins, inks, waxes (eg, candles); because it is physiologically harmless, it is used in the coloring of edible fats and oils (eg, chewing gum, confectionery, egg white, gelatin), and for cosmetics, liniments, lotions, mouthwashes, and perfumes. In the usual sense of a dye, it is used to color leather, where it exhibits good penetrating power and is especially light-stable.

Chemically pure chlorophyll is very difficult to prepare; therefore the commercial product, like that found in nature, is a mixture along with several colored substances of the carotenoid family. The main components of the natural mixture have been designated chlorophyll a and chlorophyll b, in a ratio of approximately 3 to 1, along with yellow, orange, and red bodies. The excellent hiding power of the green chlorophylls usually mask the rest whose presence is unknown until the chlorophyll is destroyed, as in the case of autumn leaves.

RUSSELL E. FARRIS
Sandoz Colors & Chemicals

W.F. Legget, *Ancient and Medieval Dyes*, Chemical Publishing Company, New York, 1944.

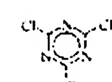
A.G. Perkin and A.E. Everest, *The Natural Organic Colouring Matter*, Longmans, Green and Co., New York, 1918.

F. Mayer, *The Chemistry of Natural Coloring Matters*, ACS Monograph No. 89, translated and revised by A.H. Cook, Reinhold Publishing Co., New York 1943.

DYES, REACTIVE

Reactive dyes are colored compounds that contain functional groups capable of forming covalent bonds with active sites in fibers such as hydroxyl groups in cellulose, amino, thiol, and hydroxyl groups in wool or amino groups in polyamides. This bond formation between the functional group and the substrate results in high wetfastness properties. These dyes differ fundamentally from other types of dyes that owe their wetfastness to physical adsorption or mechanical retention (see Dyes and dye intermediates). The principal commercial applications of reactive dyes are in the dyeing of cellulose, wool, and nylon, either individually or as components of fiber blends. They are also used in dyeing silk, hair and leather (see Dyes, application and evaluation).

Intensive research on the reaction of soda cellulose with cyanuric chloride (1) led to a useful industrial method for the production of dyeings in which a covalent bond was formed between the dye and the fiber. This development resulted in the introduction of the first range of reactive dyes for cellulose in 1956. These dyes contained either a monochloro- or a dichloro-s-triazine moiety, and were marketed as the Procion H (ICI) or Procion M (ICI) ranges.



(1)

Kokai (Jpn. Unexamined Patent Publication) No. 6-73320

Title of the Invention: Recording Liquid

Publication Date: March 15, 1994

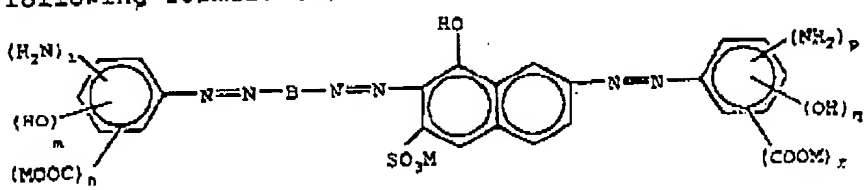
Patent Application No. 3-294625

Filing Date: November 11, 1991

Applicant: Mitsubishi Chemical Ltd.

SCOPE OF CLAIM FOR PATENT

A recording liquid comprising an aqueous medium and at least one dye selected from dyes represented by the following formula [I]:



[I]

(wherein B represents a phenylene group which may be substituted or a naphthylene group substituted by SO_3M group, l and p each represents 0 or 1, m and q each represents 1, 2 or 3, n and r each represents 0 or 1, and M represents an alkali metal, NH_4 or an organic amine salt).

DETAILED DESCRIPTION OF THE INVENTION

[Field of Utilization in Industry]

The present invention relates to a recording liquid, more specifically, the present invention relates to a recording liquid suitable for ink jet recording.

[Background Art]

A so-called ink jet recording method is used in practice, where droplets of a recording liquid comprising a water-soluble dye such as direct dye or acid dye are splashed from a fine ejection orifice to perform recording.

This recording liquid must satisfy the requirements such that fast fixing is attained on PPC (plain paper copier) paper such as electrophotographic paper, or recording paper generally used for business, such as fan fold paper (continuous paper for a computer or the like), the printed matter has good printing quality, that is, the printed letter is not blurred and has a clear contour, and stability during storage as a recording liquid is excellent. Therefore, the solvent which can be used is strictly limited.

On the other hand, the dye for recording liquid is required to have sufficiently high solubility in those limited solvents, be stable during storage as a recording liquid for a long period of time, and give a printed image having high density and excellent in water resistance and light fastness. However, it is difficult to satisfy these many requirements at the same time. For this purpose, various methods have been proposed (for example, Japanese Unexamined Patent Publication Nos. 55-144065, 57-30773, 57-207660, 58-147470, 62-190269, 62-190271, 62-190272, 62-250082, 62-246975, 62-257971, 62-288659, 63-8463, 63-22867, 63-22874, 63-30567, 63-33484, 63-63764, 63-105079, 64-31877, 1-93389, 1-210464 and 2-140270) but these cannot fully satisfy the requirements on the market.

(Problems to be Solved by the Invention)

The object of the present invention is to provide a recording liquid for ink jet recording, writing and the like, which ensures good printing quality when recorded on plain paper, gives a recorded image having high density and excellent in water resistance and particularly in light fastness, and exhibits good stability during storage for a long period of time.

(Means to Solve the Problems)

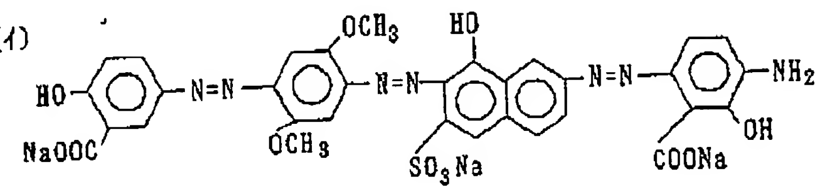
The present inventor has confirmed that when a specific black dye is used as a recording liquid component, the above-described object can be attained, and has accomplished the present invention. More specifically, the gist of the present invention resides in a recording liquid comprising at least one dye represented by formula [I] in claim 1. The present invention is described in detail below. Examples of the phenylene group represented by B in formula [I] include an SO_3M group, a COOM group, a methyl group, a methoxy group and an acylamino group such as lower alkylcarbonylamino group.

Examples of the organic amine salt represented by M include a group where 3 or 4 hydrogen atoms of an ammonium group are substituted by an alkyl group having from 1 to 4 carbon atoms and/or a hydroxyalkyl group having from 1 to 4 carbon atoms. Specific examples of these dyes include azo dyes having the following structures (イ) to (ヌ).

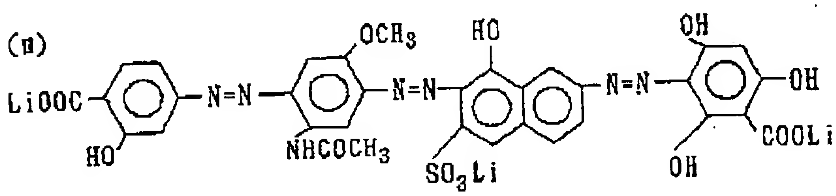
The azo dye represented by formula [I] itself can be produced through diazotization and coupling process according to a known method [see, for example, Yutaka Hosoda, Shin Senryo Kagaku (New Dye Chemistry), Gihodo (December 21, 1973)]. The content of the dye of formula [I] in the recording liquid is preferably from 0.5 to 5 wt%, more preferably on the order of from 2 to 4 wt%.

The solvent for use in the recording liquid of the present invention preferably contains water and a water-soluble organic solvent such as ethylene glycol, propylene glycol, butylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol (#200), polyethylene glycol

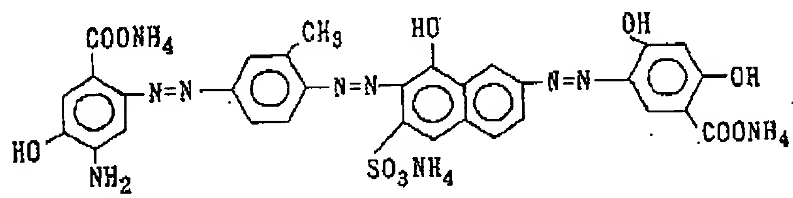
(イ)



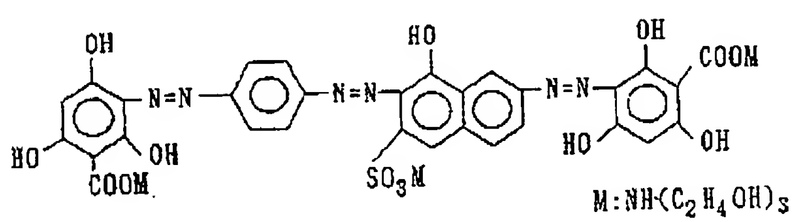
(ロ)



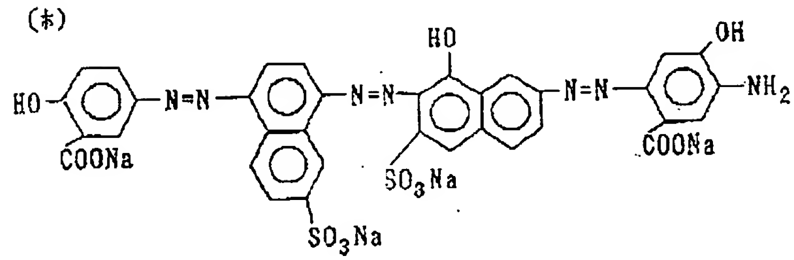
(ハ)



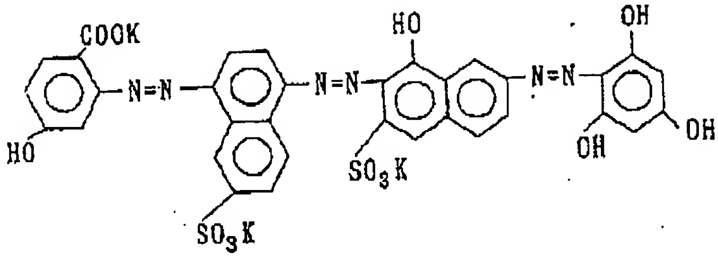
(ニ)



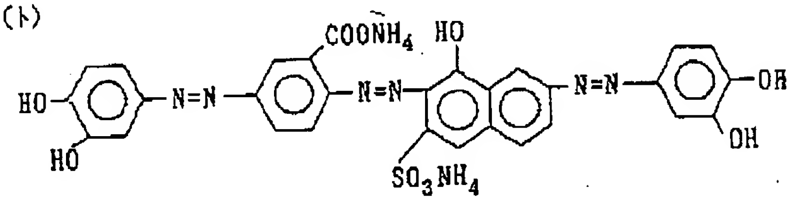
(ホ)



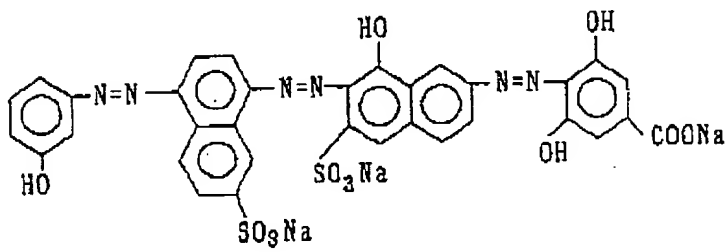
(ヘ)



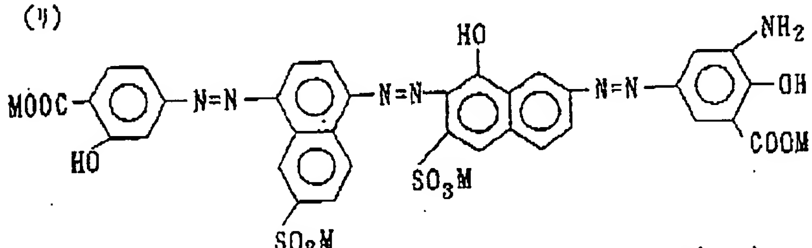
(ト)



(チ)

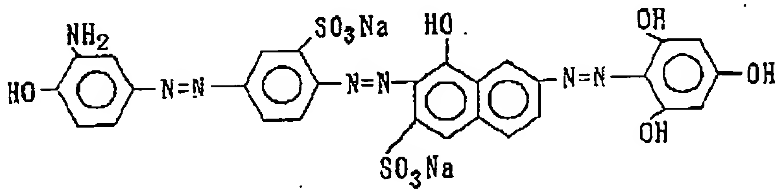


(リ)



M: $HOH_4C_2N(CH_3)_3$

(ヌ)



(#400), glycerin, N-methyl-pyrrolidone, N-ethyl-pyrrolidone, 1,3-dimethyl-imidazolidinone, ethylene glycol monoallyl ether, ethylene glycol monomethyl ether and diethylene glycol monomethyl ether. The water-soluble organic solvent is usually used in the range from 10 to 50 wt% based on the entire amount of the recording liquid. On the other hand, water is used in the range from 45 to 89.5 wt% based on the entire amount of the recording liquid.

The recording liquid of the present invention can be more improved in the quick drying property after printing and the printing quality by adding a compound selected from urea, thiourea, biuret and semicarbazide in an amount of 0.1 to 10 wt%, preferably from 0.5 to 5 wt%, based on the entire amount of the recording liquid, or by adding from 0.001 to 5.0 wt% of a surfactant.

[Examples]

The present invention is described in greater detail below by referring to Examples, however, the present invention is not limited to these Examples insofar as the gist is observed.

Example 1:

To 25 parts by weight of ethylene glycol monoallyl ether, 22 parts by weight of ethylene glycol and 3.5 parts by weight of the dye of formula (1), water was added to make a total amount of 100 parts by weight. This composition was thoroughly mixed and dissolved and after filtering through a Teflon filter having a pore size of 1 μm under pressure, subjected to a degassing treatment by a vacuum pump and an ultrasonic washer to prepare a recording liquid. Using the obtained recording liquid, ink jet recording was performed on electrophotographic paper

(produced by Fuji Xerox) by an ink jet printer (HG-3000, trade name, produced by Epson). The results of various evaluations performed by the following methods (a), (b) and (c) are shown below.

(a) Light Fastness of Recorded Image:

The recorded paper was irradiated for 100 hours using a xenon fademeter (manufactured by Suga Shikenki). The discoloration after irradiation was small.

(b) Water Resistance of Recorded Image:

After dipping the recorded paper in water for 24 hours, blurring of the image was examined. The blurring of image was little and the reduction of density was small.

(c) Storage Stability of Recording Liquid:

The recording liquid was enclosed in a Teflon container and stored at 5°C and 60°C for 1 month and thereafter, the change was examined. Precipitation of insoluble matters was not observed.

Example 2:

To 10 parts by weight of glycerin, 10 parts by weight of ethylene glycol and 5 parts by weight of the dye of formula (ロ), water was added to make a total amount of 100 parts by weight. This composition was processed by the method described in Example 1 to prepare a recording liquid and various evaluations of (a) to (c) of Example 1 were performed. Then, good results were obtained in any evaluation similarly to Example 1.

Example 3:

To 5 parts by weight of diethylene glycol monobutyl ether, 15 parts by weight of glycerin and 2 parts by weight of the dye of formula (ハ), water was added to make a total amount of 100 parts by weight. This composition was

processed by the method described in Example 1 to prepare a recording liquid and various evaluations of (a) to (c) of Example 1 were performed. Then, good results were obtained in any evaluation similarly to Example 1.

Examples 4 to 10:

Recording liquids were prepared by the method described in Example 1 except for using the dyes of formula (ニ) to (ヌ) in place of the dye of (イ) used in Example 1, and various evaluations of (a) to (c) of Example 1 were performed. Then, good results were obtained in any evaluation similarly to Example 1.

[Effects of the Invention]

The recording liquid of the present invention is used for ink jet recording and writing tool and when used in recording on plain paper, gives a recorded image excellent in printing density, light fastness and water resistance. In addition, the recording liquid of the present invention exhibits good storage stability.

Textile Dyeing and Coloration

by

J. R. Aspland
Clemson University

AMERICAN ASSOCIATION OF TEXTILE CHEMISTS AND COLORISTS
P.O. Box 12215, Research Triangle Park, N.C. 27709, USA
Tel: 919-549-8141; Fax: 919-549-8933; e-mail: aatcc.org

ISBN 0-9613350-1-7

Pr

This book is the final integrat
Richard Aspland which were p
ist between October 1991 and

One of the purposes of the c
ject of fiber coloration in a ma
extend the information given
AATCC in 1981. Additionally,
ner as to progressively increas
ters so that one of little prior k
tent, yet continuously add to
of dyeing theory and applicat

The coloration of textile fib
considering the diversity of
tions; the array of wet proces
end-uses and fastness requi
work done by researchers an
standing dyeing theory. It is
theory that appropriate appl
the available equipment can
ing. Also, through the unders
shooting and problem solvin
out a good understanding c
mains an "art" and not a "sc

This book has been divide
each of the dye-fiber substan
of important color-related t
ceding parts. An inspection
tents shows that some deal
the fiber surfaces and into
chemical technology associa
egories. Some readers will b
mechanisms.

Dr. Aspland brings the re
ing manufacturing, research
of Textiles, Fiber and Polym
1981, Dr. Aspland was a par

ɘ fabric are not batched too
· but evenly throughout for
the alkali and reactive dye
. then be efficiently washed
v flow of hot or cold water.
conventional batch or con-
is easier to make adds to a

yeing greige goods with or
and and appearance while
antially.
lar benefits to those dyeing
se their expensive, high tem-
hines for dyeing the polyes-
for lengthy reactive dyeing
equire temperatures even as

and the unfixed, hydrolyzed
er a possibility of leveling or
a reactive dyeing is unsatis-
te what steps must be taken

out 20–40% in depth of shade
sis of the dye-fiber bond with
0F).
complete chemical stripping
: in one of the following four
wed by oxidation, oxidation
iction. An example is given

present, it is first desirable to
atment of the dyeings at the
: liter EDTA solution followed,
: liter each of caustic soda and
soda ash may be substituted
ɘ treatment with sodium hy-
re stripping, and all traces of

chemicals should be removed prior to any redyeing attempts on a sample of the stripped goods.

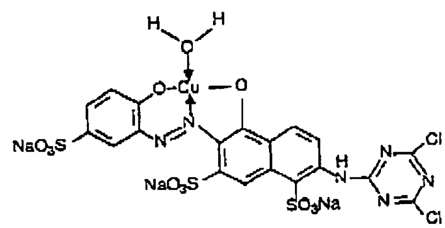
9.6 Chemisty of Reactive Dyes

Reactive dyes, apart from easily recognizable reactive functional groups, have structures which are not very different from those of acid dyes and direct dyes in several important respects.

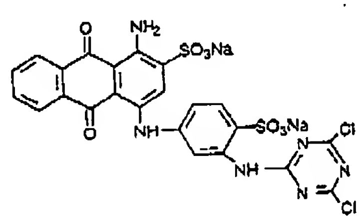
Direct dye molecules tend to be larger, more linear, and somewhat less brightly colored than acid dye molecules with specific components such as J-acid derivatives being much in evidence. Otherwise, it might be tricky to tell acid and direct dye molecules apart.

9.6.1 Chromophores

Reactive dyes all rely on many of the same chromophoric groups as acid and direct dyes for their color, although the azo chromophore, –N=N–, is by far the most important, cf. Fig 9.1a, 9.3, 9.4 and 9.6.



a) Metallized monoazo - C.I.Reactive Red 6



b) Anthraquinonoid - C.I. Reactive Blue 4

Fig. 9.1. Typical dichlorotriazinyl reactive dyes (highly reactive).

Any of the following chromophores may be used: mono and disazo (metallized and unmetallized), triphenoxazine and phthalocyanine (see section 3.2.3). Acid and reactive dyes, especially bright blues, often depend on anthraquinone derivatives (see Fig. 9.1b and section 15.2.2 on disperse dyes). All reactive dyes contain sodium sulfonate groups for solubility, and dissolve in water to give colored sulfonate anions and sodium cations. Most reactive dyes have from one to four of these sulfonate groups.

Reactive dye molecules, however, do have several specific structural (reactive) features of their own. These are of two principal types: carbon-nitrogen (heterocyclic) ring structures and masked vinyl sulfones.

9.6.2 Carbon-Nitrogen Rings

The reactive structures (R), of which some important examples are shown in Fig. 9.1, are attached to the rest of the dye molecule by bridging groups (B) such as imino, –NH–, substituted imino and amide linkages, –NHCO–.

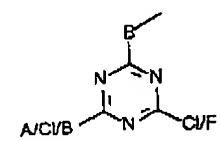
The leaving groups (X) are attached initially at carbon atoms adjacent to a ring nitrogen. The carbon atoms are positively polarized and come under attack from nucleophiles such as the cellulosate and hydroxide anions. The outcome is the nucleophiles substitute themselves in place of the leaving groups, which are expelled carrying an electron with them, usually as inert anions.

Potential leaving groups (X) include chloro groups, fluoro groups, –F, and methyl sulfonyl groups, CH_3SO_2–, arranged in order of decreasing importance. These leaving groups may be called "nucleofugic" because they take refuge by running away from nucleophiles.

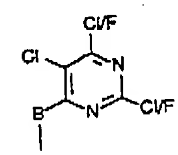
This might be an appropriate place to list the names and abbreviations for a number of these reactive species, arranged in order of gradually increasing reactivity: trichloropyrimidine, TCP; monochlorotriazine, MCT; masked vinyl sulfones, VS; monofluorotriazine, MFT; difluorochloropyrimidine, FCP; and dichlorotriazine, DCT. All the heterocyclic compounds are shown in Fig. 9.2.

9.6.3 Vinyl Sulfones

These reactive groups are normally transients, and are masked by water solubilizing leaving groups and their name is abbreviated to



a) s. triazine



b) pyrimidine

Fig. 9.2. Selected heterocyc
or substituted amino (not a c
–NH–.

(VS). Vinyl sulfone grou
this group is rarely if eve
found is generally the fu

$-SO_2-$

Whether the structure ir
depends on the pH.

The bridging group (I
ture, which withdraws
in the presence of alkal
drogen ion (from the car
the hidden vinyl group

$-SO_2-CH_2-C$

The bisulfate ion is r
pending on pH. The vi
whatever nucleophiles
nally adds back the hy

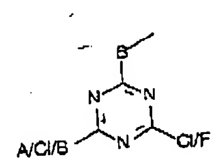
; may be used: mono and
iphenoxazine and phthalo-
:tive dyes, especially bright
erivatives (see Fig. 9.1b and
active dyes contain sodium
ssolve in water to give col-
ns. Most reactive dyes have
ups.
have several specific struc-
ese are of two principal types:
ructures and masked vinyl

ome important examples are
rest of the dye molecule by
NH–, substituted imino and

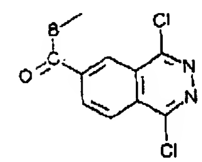
initially at carbon atoms ad-
toms are positively polarized
hiles such as the cellulosate
is the nucleophiles substitute
ups, which are expelled carry-
inert anions.
chloro groups, fluoro groups,
SO_2–, arranged in order of de-
ing groups may be called
ge by running away from nu-

e to list the names and abbre-
e species, arranged in order of
trichloropyrimidine, TCP;
sked vinyl sulfones, VS;
chloropyrimidine, FCP; and
cyclic compounds are shown

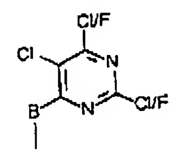
transients, and are masked by
d their name is abbreviated to



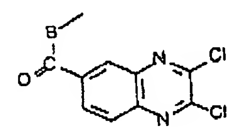
a) s. triazine



c) 2,3 – benzodiazine



b) pyrimidine



d) 1,4 – benzodiazine

Fig. 9.2. Selected heterocyclic reactive groups; A = terminal group, alkoxy or substituted amino (not a chromophore) and B = bridging group, normally –NH–.

(VS). Vinyl sulfone groups are actually written: $-SO_2-CH=CH_2$, but this group is rarely if ever found in a reactive dye product. What is found is generally the functional group:

$$-SO_2-CH_2-CH_2-OSO_3^-(H^+ \text{ or } Na^+)$$

Whether the structure includes the hydrogen ion or the sodium ion depends on the pH.

The bridging group (B) is the sulfone, $-SO_2-$, portion of the structure, which withdraws electrons from the rest of the group so that, in the presence of alkali, the leaving group (X) departs with a hydrogen ion (from the carbon next to the sulfone group) and unmasks the hidden vinyl group:

$$-SO_2-CH_2-CH_2-OSO_3^- \rightarrow -SO_2-CH=CH_2 + HSO_4^- \qquad \text{Eq. 9.1}$$

The bisulfate ion is more or less neutralized to a sulfate ion, depending on pH. The vinyl group immediately begins to add back whatever nucleophiles are around—e.g., OH^- and Cell–O—and finally adds back the hydrogen ion as well.